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Date of Deposit: April 27, 2005

G. Peter Nichols, Reg. No. 34,401

Name of Applicant, Assignee or  
Registered Representative

Signature

**Case No. 10908/5**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Appln. of: Ahern et al.  
Appln. No.: 10/658,635  
Filed: September 8, 2003  
For: Recovery of Metals from  
Jarosite-Containing Materials

Examiner: Andrews

Art Unit: 1742

Attorney Docket No: 10908/5

**SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENTS**

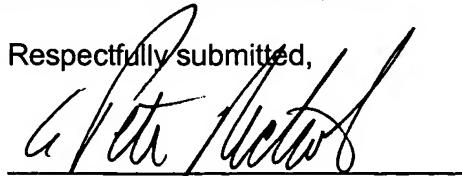
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

Transmitted herewith is a certified copy of the following priority document for the above-named U.S. application:

1. South African Provisional Patent Application No. 2001/1927, filed March 8, 2001;
2. PCT Application No. PCT/ZA02/00024 filed March 6, 2002.

Respectfully submitted,



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# Sertifikaat

REPUBLIEK VAN SUID AFRIKA

PATENT KANTOOR  
DEPARTEMENT VAN HANDEL  
EN NYWERHEID



# Certificate

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE  
DEPARTMENT OF TRADE AND  
INDUSTRY

Hiermee word gesertifiseer dat  
This is to certify that

the documents annexed hereto are true copies of:

Application forms , P2, provisional specification and drawing of South African Patent Application No. 2001/1927 as originally filed in the Republic of South Africa on 8 March 2001 in the name of BILLITON SA LIMITED for invention entitled: "RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS".

CERTIFIED COPY OF  
PRIORITY DOCUMENT

en te

PRETORIA

in die Republiek van Suid-Afrika, hierdie

in the Republic of South Africa, this

dag van

23rd

day of

March 2005

Registrar of Patents

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF  
RECEIPT

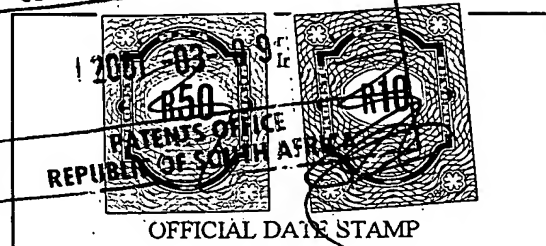
(Section 30(1) - Regulation 22)

REGISTRAR OF THE COURT OF  
COMMISSIONER OF PATENTS

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.

21	01	20011927
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FULL NAME(S) OF APPLICANT(S)

71	BILLITON SA LIMITED
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ADDRESS(ES) OF APPLICANT(S)

200 HANS STRIJDOM DRIVE, RANDBURG, 2194
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TITLE OF INVENTION

54	RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS
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Priority is claimed as set out on the accompanying Form P2.

The earliest priority claimed is :

This application is a patent of addition to Patent Application No.	21	01
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This application is a fresh application in terms of section 37 and based on Application No.	21	01
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THIS APPLICATION IS ACCOMPANIED BY:

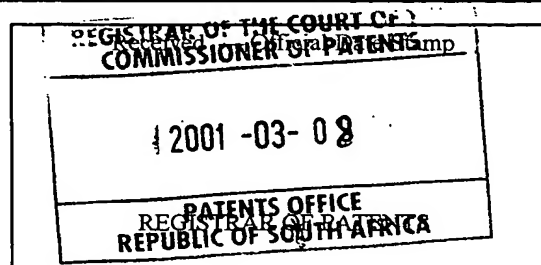
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|-------------------------------------|----|--|
| <input checked="" type="checkbox"/> | 1  | A single copy of a provisional specification of 12 pages                 |
| <input type="checkbox"/>            | 2  | Two copies of a complete specification of ..... pages                    |
| <input checked="" type="checkbox"/> | 3  | 1 sheet of Informal Drawings   |
| <input type="checkbox"/>            | 4  | ..... sheets of Formal Drawings  |
| <input type="checkbox"/>            | 5  | Publication particulars and abstract (Form P8 in duplicate)              |
| <input type="checkbox"/>            | 6  | A copy of Figure ..... of drawings (if any) for the abstract             |
| <input type="checkbox"/>            | 7  | Assignment of Invention  |
| <input type="checkbox"/>            | 8  | Certified priority document(s) Number(s)                                 |
| <input type="checkbox"/>            | 9  | Translation of priority document(s)                                      |
| <input type="checkbox"/>            | 10 | An assignment of priority rights   |
| <input type="checkbox"/>            | 11 | A copy of the Form P2 and the specification of SA Patent Application No. |
| <input type="checkbox"/>            | 12 | A declaration and power of attorney on Form P3                           |
| <input type="checkbox"/>            | 13 | Request for ante-dating on Form P4                                       |
| <input type="checkbox"/>            | 14 | Request for classification on Form P9                                    |
| <input checked="" type="checkbox"/> | 15 | Form P2 in duplicate   |

21	01
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74	ADDRESS FOR SERVICE: McCALLUM, RADEMEYER & FREIMOND, Maclyn House, June Avenue, Bordeaux P.O. Box 1130, Randburg, 2125
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Dated this 8<sup>th</sup> day of March 2001.

McCALLUM, RADEMEYER & FREIMOND  
PATENT AGENTS FOR APPLICANT(S)



REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

## REGISTRAR OF PATENTS

Official Application No.			Lodging date: Provisional			Acceptance date:		
21	01	20011927	22	8 MARCH 2001		47		
International classification			Lodging date: Complete			Granted date:		
51			23					
Full name(s) of applicant(s)/Patentee(s)								
71	BILLITON SA LIMITED							
Applicant(s) substituted:						Date Registered:		
Assignee(s):						Date Registered:		
71								
Full name(s) of inventor(s)								
72	AHERN, Noelene ; SCHAEKERS, Jozef, Marie							
Priority claimed		Country		Number		Date		
Note:  Use International  Abbreviation for Country	33	NONE	31	NONE	32	NONE		
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Title of Invention:								
54	RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS							
Address of applicant(s)/patentee(s)								
200 HANS STRIJDOM DRIVE, RANDBURG, 2194								
Address for Service:								
74	McCALLUM, RADEMEYER & FREIMOND, Maclyn House, June Avenue, Bordeaux, Randburg • P.O. Box 1130, Randburg 2125							
Patent of Addition No.			Date of any change:					
61								
Fresh Application based on:			Date of any change:					

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

**PROVISIONAL SPECIFICATION**

(Section 30(1) - Regulation 27)

**OFFICIAL APPLICATION NO**

21	01	<b>20011927</b>
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**LODGING DATE**

22	<b>8 MARCH 2001</b>
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**FULL NAME(S) OF APPLICANT(S)**

71	<b>BILLITON SA LIMITED</b>
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**FULL NAME(S) OF INVENTOR(S)**

72	<b>AHERN, Noelene ; SCHAEKERS, Jozef, Marie</b>
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**TITLE OF INVENTION**

54	<b>RECOVERY OF METALS FROM JAROSITE-CONTAINING MATERIALS</b>
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## BACKGROUND OF THE INVENTION

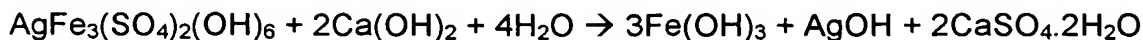
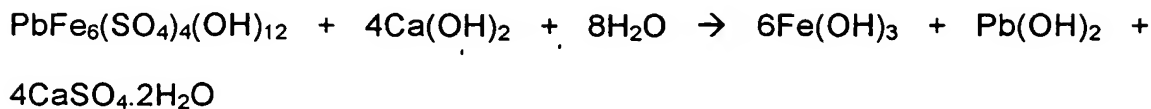
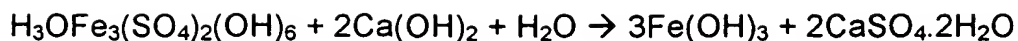
This invention relates to the recovery of metals from jarosite-containing materials.

The leaching of certain metals. e.g. silver (Ag), lead (Pb) and zinc (Zn) using  
5 brine leaching, is well known.<sup>(1,2,3,4,5)</sup> The ease of solubilising these metals depends on the refractory nature of the material treated.

To improve recoveries from refractory materials by brine leaching, a combined high temperature oxidation process in combination with acidic brine leaching has been proposed.<sup>(4)</sup> A concentrate containing silver, mostly in sulfide  
10 minerals, yielded only 50 % Ag dissolution in a  $\text{FeCl}_3$  brine leach. By leaching the concentrate at temperatures above  $100^\circ\text{C}$  with a high oxygen partial pressure in an acidic  $\text{NaCl}$  or  $\text{CaCl}_2$  medium, the Ag recovery was increased to above 95 %.

Brine leaching alone is not effective in solubilising metals included in or  
15 encapsulated by jarosite or other similar iron hydroxy sulfate compounds since these compounds must first be decomposed.

Decomposition of jarosites in alkaline medium is well known. Jarosites produced during pressure leaching of zinc concentrates were decomposed by treating the residues with a lime slurry at  $90^\circ\text{C}$ .<sup>(7)</sup> The following reactions  
20 were proposed to describe the reactions for hydronium jarosite, plumbojarosite and argentojarosite respectively:



5 After liberation, Ag was subsequently recoverable by cyanidation.<sup>(7)</sup>

Destruction of jarosites produced in pressure leaching using lime at 85°C to 90°C using an approximately stoichiometric quantity of lime, followed by cyanidation, improved Ag recoveries from less than 5 % to more than 97 %.<sup>(9)</sup>

10 NaOH has also been used to facilitate alkaline decomposition of jarosite-type materials before cyanidation.<sup>(8)</sup>

Leaching of jarosite-containing materials in an acidic brine medium of  $\text{CaCl}_2$  at a temperature above the boiling point of the solution and elevated pressures, in the presence of lime or another suitable alkali to maintain the pH between 1.5 and 3.5, has been proposed to recover metals from jarosite.<sup>(6)</sup> Although  
15 this method was successful to recover Ag and Pb from jarosites the use of high pressures and temperatures is not always desirable.

It seems obvious that if metal recovery from jarosites is required, an alkaline pretreatment followed by cyanidation is a generally accepted and suitable method. However, cyanide has environmental disadvantages, and in some  
20 cases, cyanide consumption is too high for such a process to be economical, particularly in the presence of base metals like Cu, and sulfides.

Also, it is implied that jarosite-containing materials can be pretreated in an alkaline medium to liberate certain metals, and that once the metals are in suitable forms, brine leaching can be used to solubilise them. However, this treatment implies the use of a liquid/solid separation step between the alkaline decomposition stage and the acidic brine solubilisation, and additional process steps and costs. There would be advantages to eliminating this liquid/solid separation, by carrying out the alkaline decomposition in brine medium followed immediately by acidification to solubilise the required metals. Also, the alkaline decomposition step is shown to be facilitated in a brine solution.

#### SUMMARY OF INVENTION

The invention provides a method to dissolve metals from jarosite or other iron hydroxy sulfate containing material by:

- a) alkaline treatment of the material in a brine solution to facilitate jarosite decomposition, and
- b) acidification of the brine slurry to solubilise the liberated metals.

The method may include the step of adjusting the pH of the brine slurry to remove solubilised iron or other impurities from the slurry followed by the step of separating the metal-containing brine solution and the solid residue from each other.

The metal values can be removed from the brine solution by any appropriate means, e.g. cementation, ion exchange, solvent extraction, electrowinning or



precipitation. After metal recovery, the barren brine liquor may be recycled to the alkaline treatment stage. A bleed stream may be introduced to control impurities, and additional NaCl and water may be added on recycle to compensate for any losses.

- 5 Preferably the temperature in the alkaline treatment stage is between 30°C and 100°C.

Alkali may added to the brine solution in the form of lime, NaOH, LiOH or any other suitable alkali, or any combination thereof.

- 10 Preferably the brine concentration is between 100 g/l NaCl and saturation levels, or the equivalent of any other soluble chloride salt.

The temperature in the acidic brine leach stage may be between 30°C and 100°C.

The pH of the acidic brine leach stage is preferably less than 6.

The method may be used particularly for the recovery of silver.

- 15 BRIEF DESCRIPTION OF THE DRAWING

The invention is further described by way of examples with reference to the accompanying drawing which is a flow chart representation of the method of the invention.

## DESCRIPTION OF PREFERRED EMBODIMENT

Referring to the accompanying drawing, a silver and jarosite-containing residue (10) is typically obtained by subjecting a silver bearing material to a leaching process (e.g. bioleaching or pressure leaching) or by subjecting a silver and iron containing liquor to a precipitation process (e.g. iron removal).

The residue is subjected to an alkaline pretreatment in brine medium (12). The liquid to solid ratio should be sufficient to ensure ease of operation and to ensure that no solubility constraints exist for the silver. The brine solution should contain from 100 g/l NaCl to saturation levels, preferably 200 g/l to 300 g/l. The brine solution may contain various impurities, including sulfate. Sulfate levels of up to 10 g/l may be acceptable, but less than 5 g/l are expected if lime is used as the alkali. The slurry should be maintained at a temperature of 30°C to 100°C, preferably 50°C – 90°C.

An alkali (14) such as lime is added to the slurry either to maintain an alkaline pH (>7), preferably greater than or equal to 9, and less than 13, or at a fixed addition based on the stoichiometry of the alkaline decomposition reaction.

The reaction is allowed to continue for a time depending on the composition of the material and the reaction temperature and pH. Usually a few hours is sufficient but more than 24 hours may be required in some cases, particularly in the lower pH or temperature ranges.

The alkaline brine slurry is then acidified (step 16) without any intermediate liquid/solid separation by the addition of any suitable acid (18), preferably HCl

or  $\text{H}_2\text{SO}_4$  to a pH most suitable for the metal that is to be dissolved. For Ag, the pH should be less than 6 and greater than 0.1, preferably between 1 and 3.

5 The temperature of the acidic brine leach can be the same as that used in the alkaline pretreatment step ( $30^\circ\text{C} - 100^\circ\text{C}$ ) and is preferably  $70^\circ\text{C} - 90^\circ\text{C}$ .

As for the alkaline pretreatment stage, the residence time required for the acid leaching stage is variable, but is not expected to be longer than 8 hours.

10 An iron removal stage 20 may be included where the pH of the slurry is increased slightly by the addition of a suitable alkali 22, to precipitate iron. The pH should be less than 5.

After liquid/solid separation (24) to remove the solid residue 26, Ag is recovered by any suitable means, in this case, cementation 28, with Fe scrap 30. The Ag product is removed by liquid/solid separation (34) and the barren brine solution 36 is recycled to the alkaline pretreatment step (12).

15 Part of the brine solution 36 may be removed as a bleed stream 38 to control impurity build up. Also it may be necessary to add NaCl (40) and water 42 to make up the stream recycled to the stage 12.

### **Example 1**

20 A residue containing about 70 % of the Ag in jarosite was slurried with a 260 g/l NaCl solution at  $80^\circ\text{C}$  at a liquid to solid ratio of 10:1. The natural pH of

the slurry ranged between 1.8 and 2.4. After leaching for 6 hours, the Ag dissolution was 22 %.

This indicates that brine leaching alone is not sufficient to recover Ag from jarosite-type materials.

## 5     **Example 2**

A residue containing about 70 % of the Ag in jarosite was slurried with a 260 g/l NaCl solution at 70 °C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to 145 kg  $\text{Ca(OH)}_2$  per ton of sample, based on a stoichiometric excess of 20 %, and the slurry was agitated for 2 hours. The  
10     slurry was then acidified to pH 2 by adding 97 kg  $\text{H}_2\text{SO}_4$  per ton of sample, and agitated for a further 5 hours. Ag dissolution of 94 % was obtained.

This illustrates the process of the invention using a fixed amount of alkali.

## **Example 3**

A residue containing about 70 % of the Ag in jarosite was slurried with a 260  
15     g/l NaCl solution at 80°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9. After 3 hours, 126 kg  $\text{Ca(OH)}_2$  per ton of sample had been consumed. The slurry was then acidified to pH 2 by adding 87 kg  $\text{H}_2\text{SO}_4$  per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 93 % was achieved.

This illustrates the process of the invention using a set pH during the alkali treatment.

#### **Example 4**

5 A residue containing about 70 % of the Ag in jarosite was slurried with a 260 g/l NaCl solution at 70°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9.5. After 4 hours, 181 kg Ca(OH)<sub>2</sub> per ton of sample had been consumed. The slurry was then acidified to pH 2 by adding 100 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 94 % was achieved.

10 This test was repeated, but excluding brine from the alkaline decomposition stage. After 24 hours, 83 kg Ca(OH)<sub>2</sub> per ton of sample had been consumed. The slurry was then acidified by adding 54 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample and allowed to react for a further 5 hours. Ag dissolution of 43 % was achieved.

15 This illustrates that the presence of brine in the alkaline decomposition stage facilitates the decomposition of jarosite.

#### **Example 5**

20 A residue containing about 70 % of the Ag in jarosite was slurried with a 260 g/l NaCl solution at 70°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to 145 kg Ca(OH)<sub>2</sub> per ton of sample, based on a stoichiometric excess of 20 %, and the slurry was agitated for 2 hours. The

slurry was then acidified to pH 2 by adding 131 kg  $\text{H}_2\text{SO}_4$  per ton of sample, and agitated for a further 5 hours.

To remove Fe from the circuit, limestone was added as a solid to establish a pH of 3.7. The solid residue was then separated from the brine solution.

5 Overall Ag dissolution of 87 % was obtained.

This illustrates the process of the invention when an iron removal stage is included.

#### **Example 6**

10 The same procedure was carried out as for example 2, except that the temperature during alkaline pretreatment was 50°C, not 70°C. Acid consumption in the acid leach step was 164 kg  $\text{H}_2\text{SO}_4$  per ton, and Ag dissolution was only 63 %.

This example illustrates the importance of temperature in the alkaline treatment stage.

#### **Example 7**

15 A residue containing about 70 % of the Ag in jarosite was slurried with a 260 g/l NaCl solution at (a) 70°C and (b) 80°C at a liquid to solid ratio of about 7:1. Lime was added as a slurry to maintain a constant pH of 9 for both tests, and the slurry was agitated until no further lime additions were necessary to  
20 maintain the set pH. The slurries were then acidified to pH 2 by adding (a) 82

and (b) 87 kg H<sub>2</sub>SO<sub>4</sub> per ton of sample respectively, and agitated for a further 5 hours.

In both cases, Ag dissolution was 93 %. However, where the alkali treatment was done at 70°C, 7.5 hours were required to complete this stage, while at 80°C, only 3 hours were required.

This example illustrates the effect of temperature and time on the proposed process.


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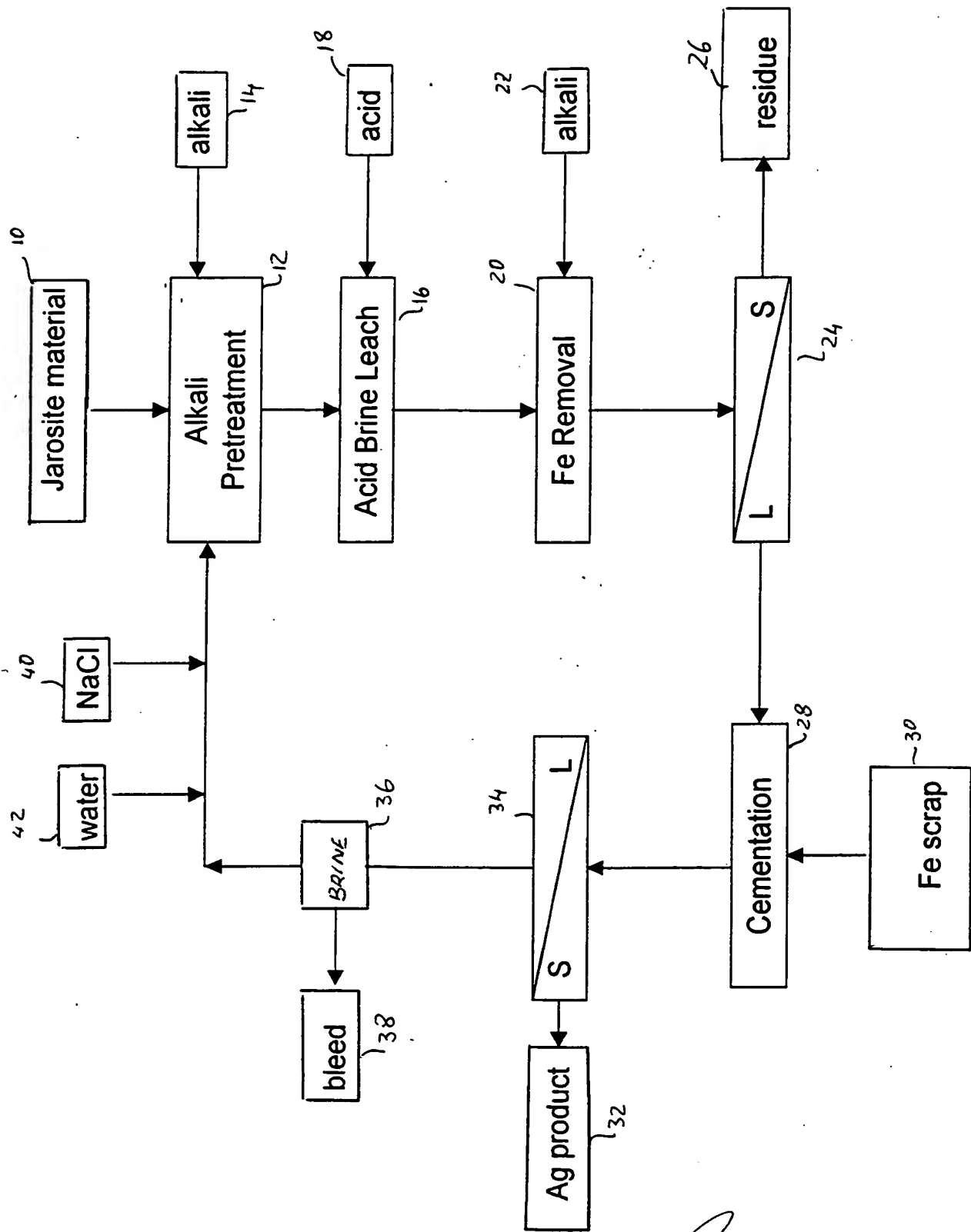


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Dated this 8<sup>th</sup> day of March 2001

  
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